University of Pittsburgh

First Annual Report

for

NASA Grant NsG-416

covering the period

1 November 1963 through 1 May 1964

Submitted by

David Halliday
Director (Acting),

Space Research Coordination Center

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First Annual Report

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1. Introduction

As in our First Semi-Annual Report, we report here on the University's entire space research program, including those portions financed by funds from Pittsburgh foundations, the Commonwealth of Pennsylvania, or NASA facilities or training grants. Activities supported under NASA Grant NsG-416 will be specifically identified.

2. Faculty Recruitment

The University has authorized the establishment of 23 new tenured faculty positions to support space-oriented research programs in science and engineering. At the time of our First Semi-Annual Report, six of these positions had been filled. As of this date, four other positions have been filled (one on a visiting basis) and three offers are outstanding. Recruitment for the remaining unfilled positions is being pursued vigorously. The four new appointees are

a. Edward C. Zipf, Jr., Assistant Professor of Physics.

Professor Zipf, who received his Ph.D. degree from the Johns Hopkins University in 1961, comes to us from the University of Colorado. His research interests are in upper atmosphere physics.

b. <u>Robert</u> <u>H.</u> <u>Gibson</u>, Associate Professor of Psychology.

Professor Gibson, who received his Ph.D. degree from
the University of Virginia in 1962, comes to us from the
Carnegie Institute of Technology. His research interest is
the study of the skin as a potential sensory organ for
receiving communicated signals.

c. <u>O.</u> <u>Kubaschewski</u>.

Professor Kubaschewski, distinguished metallurgist from
the University of London, will serve as Visiting Professor of
Metallurgy for a six-month period beginning September, 1964.
While here, he will guide the development of a research group
in the thermodynamic study of alloys.

d. <u>Donald</u> <u>Green</u>, Associate Professor of Biology.

Professor Green, who received his Ph.D. from the
University of Rochester in 1958, spent several years as a
biologist at the Oak Ridge National Laboratory and is now
completing his second year as a Research Associate at Harvard
where he is working with Professor Paul Doty. Professor
Green's research interests are in the area of microbiology.

3. <u>NASA Research Associates (NsG-416)</u>

The ten postdoctoral research associates appointed
for 1963-1964 are all pursuing stimulating programs and
appointment extensions for an additional year have been
offered to them. All have accepted, except Dr. Felix Franks
who is required to return to his home institution. Budget
considerations did not permit us to make more than four

new appointments for 1964-1965. They were selected from a large number of qualified applicants, our physics department for example having received 64 unsolicited inquiries and applications. The new research associates are in the fields of biology, mechanical engineering, crystallography and physics.

4. NASA Predoctoral Trainees [NsG(T)-70]

The ten NASA trainees who began their programs in September, 1963, are all doing very satisfactory work and their appointments have been renewed for a second year. Twelve additional appointments authorized for September, 1964, were made. Within recent weeks, however, two of the appointees have resigned, presumably to accept other offers. These appointments have been extended to other highly qualified candidates. The 20 trainees who will be in residence during 1964-1965 are distributed by field as follows: biology - 1; chemistry - 3; earth and planetary sciences - 2; chemical engineering - 2; electrical engineering - 1; mechanical engineering - 2; physics - 7; psychology - 2.

5. Capital Construction

    a. Space Research Coordination Center.

The cornerstone for this building, financed by NASA Facilities Grant NsG(F)-13, will be laid 2 June 1964, with occupancy in April 1965.

b. <u>Extension to Sarah Mellon Scaife Radiation Laboratory</u>
<u>($1,630,000)</u>.

This building, financed from private funds, is
essentially complete. Delivery of the accelerator is
expected within a few months.

c. <u>Engineering Building</u>.

Detailed planning for this $14,600,000 structure,
financed by the Commonwealth of Pennsylvania, is underway.

d. <u>Natural Sciences Building</u>.

Detailed planning for the first unit of this $7,405,000
structure, also financed by the Commonwealth of Pennsylvania,
is underway.

6. Research Reports

Progress reports from all SRCC faculty appointees
and NASA Research Associates who are in residence are
appended.

COLLISION CROSS SECTION MEASUREMENTS AND ION TECHNOLOGY
by
Wade L. Fite, Professor of Physics, and
Richard Brackmann, Research Assistant Professor of Physics
and Electrical Engineering

During the past four months progress has taken the form of transforming research plans into hardware. Acquisition and construction of equipment has taken the major share of effort. A two-stage differentially pumped vacuum system, and its accompanying electronics, etc., approach operation.

The first task for which this equipment will be used is the study of certain charge transfer reactions involving heavy ions and atmospheric gases. For these measurements, the 400-kev Van de Graaff accelerator in the physics department will be used in conjunction with the new apparatus. At present, the final construction is being made to couple the accelerator to the vacuum system. Preparation for these experiments has also involved the construction of suitable ion sources for the heavy metallic ions to be used and, in a sense, the initial steps have been taken toward the "ion technology" goals outlined in our first report.

Although the charge transfer experiments occupy the major effort, plans are already being made to convert the two-stage vacuum system into a two-stage modulated beam machine. This modification will entail construction of mass spectrometric detection equipment. It is then planned that the basic equipment now being completed can be used to carry on, more or less concurrently, (1) the charge transfer experiments, (2) development of sources of certain free radicals for neutral-neutral collision experiments pertinent to airglow excitation and (3) direct studies of collision processes with excited atoms and molecules. Supplementary support is being sought for these areas of research.

Support is also being sought for provision of more elegant equipment and operating costs for two additional programs: (1) study of the airglow excitation mechanisms and (2) study of collision processes involving atomic hydrogen. In the meantime, we await with the greatest anticipation the results of the charge transfer experiments which bear on debris motion in the upper atmosphere as well as ion propulsion and the results of experiments on electron collisions with excited molecules because of the possible application of the results to certain types of rocket experiments.

INVESTIGATION OF THE SCATTERING OF SEISMIC WAVES FROM GEOLOGIC DISCONTINUITIES

by

Walter Pilant, Associate Professor of Geophysics

The equipping of the model seismic laboratory is now complete. The laboratory is now making routine velocity and amplitude analyses of seismic pulses propagating in a variety of media. In preliminary work, it has been shown that the bonding materials (e.g., epoxy, glue, etc.) used to join dissimilar materials have a non-negligible effect upon the properties of elastic wave propagation across an interface. An analysis of the propagation characteristics of a variety of bonding materials is now underway.

The direct digitizing equipment for the model laboratory is undergoing an extensive calibration procedure at the present time. Computer programs for the analysis of the digital data have been converted to the Pittsburgh 7090 system and checked out during the calibration of the direct digitizing equipment.

During the next period of investigation, the effects of various model structures will be investigated with respect to their utility in the approximation of representative real earth structures.

THE EARTH TIDE PROGRAM
by
Robert Stoneley, Professor of Geophysics

The previous report has emphasized the importance of observations of Earth tides in providing an overall check on theories of the internal constitution of the Earth. The usual exposition of the theory does not allow for regional differences in crustal structure, and as a long-range project a regional survey of Earth tides is much to be desired. As already mentioned, a joint program with the U.S. Coast and Geodetic Survey has already been agreed upon in general terms; at the moment budgetary restrictions are hampering the development of the U.S.C. & G. S. side of the work. Meantime good progress is being made at the Pittsburgh end towards setting up an Earth tide station. The chief advances are as follows.

(1) We are in the process of closing the contract on the property involved in acquiring the site.

(2) Professor Ralph Wyckoff has spent considerable time in evaluating existing instruments, with the particular aim of testing the quality of the site in respect of stability and "noise level."

(3) Two horizontal pendulums (tilt meters) have been ordered from the Royal Observatory, Brussels, and dispatch of these is promised within a few days from now.

(4) A sensitive Lacoste-Romberg gravimeter has been ordered. This is less likely than the horizontal pendulums to be adversely affected by meteorological fluctuations.

(5) Professor Wyckoff has examined and repaired the horizontal seismographs, with their galvanometers and recording gear; these were formerly operated in the basement of the Cathedral of Learning and have been out of action for some years. They will be installed at the Earth tide station, where in the first instance they will be used in site tests.

CURRENT PROJECTS IN GENERAL RELATIVITY
by
Alan H. Thompson, Assistant Professor of Mathematics

The group whose work is here reported consists of myself and two research students: Mr. R. Roman and Mr. R. Reynolds.

Mr. Roman is continuing his work on the problems of topology in general relativity. With Mr. Reynolds I am seeking generalisations of results of R. P. Kerr on groups of Killing Motions [R. P. Kerr, J. Math. Mech. 12, 33 (1963); R. P. Kerr, Tensor 12, 54 (1962)].

The work on CONFORMAL KILLING VECTORS noted in the last report is now more or less complete. Results previously established for conformal motions in a vacuum space-time have now been extended to more general four-dimensional riemann spaces.

An examination of interior solutions of Type D in the Petrov classification has been undertaken. This is motivated by the recent work of Newman and Janis on the Kerr-metrics. They interpret the solution of Type D found by Kerr as the gravitational field exterior to a rotating ring. It would be interesting to construct interior solutions (solutions to the gravitational field within matter) which could be fitted to the Kerr solution. With this in mind I have considered a space of Type D with an energy-momentum tensor of a perfect fluid, and examined the properties of the time-like congruence which constitutes the stream-lines of the fluid.

A series of introductory lectures on the use of exterior differential forms in relativity has been given to the Relativity Seminar of E. T. Newman; this will continue through the next trimester.

Dr. Gareth Williams (University of Florida) has joined the group for two months and is continuing his work on Rigid Motion in Relativity.

The following papers are in preparation:

(1) On Conformal Motion in the Space-Time of Relativity.

(2) A Note on the Petrov-Types of Certain Space-Times.

UDP-GLUCURONIC ACID CARBOXY-LYASE FROM CRYPTOCOCCUS LAURENTII (Y 1401)

by
Helmut Ankel, NASA Research Associate in Biology

Uridine 5-(D-xylosyl pyrophosphate) "UDPxylose" has been isolated from dried cells of Cr. laurentii. In addition, crude soluble extracts obtained by disintegration of the organism in a French pressure cell catalyze the formation of "UDPxylose" from uridine 5-(D-glucosyluronic acid pyrophosphate) "UDPGA" [Ankel, et al, Am. Chem. Soc. Abstr. 145, 5C (1963)]. The activity of these extracts is increased by addition of NAD and abolished by the action of NAD glycohydrolase (3.2.2.5). "UDPGA" carboxy-lyase has been partially purified by fractionation of the crude extract with $MnCl_2$ and $(NH_4)_2SO_4$. The enzyme has a pH optimum of 7.4 and a K_m at 37°C of 10^{-3} M. The purified enzyme has an absolute requirement for NAD with half-maximal activation at 10^{-6} M. At a NAD concentration of 3×10^{-3} M an equal concentration of NADH inhibits the enzyme 90 per cent. The enzyme is not activated but is inhibited by NAD analogs in which nicotinamide is replaced by: pyridyl-3-aldehyde, 3-acetylpyridine, 3-ethyl pyridyl ketone, thionicotinamide or ethyl nicotinate. Nicotinamide-hypoxanthine-dinucleotide and α-NAD neither activate nor inhibit. The observed requirement for NAD and the known ease of decarboxylation of β-keto-acids are consistent with the hypothesis that the decarboxylation of "UDPGA" involves the transient formation of a carbonyl intermediate by oxido-reduction at C-4.

STUDIES ON THE STRUCTURAL PROPERTIES OF WATER
AND AQUEOUS SOLUTIONS
by
Felix Franks, NASA Research Associate in Chemistry

1. The Properties of Water-Urea-Hydrocarbon Systems.

The model described in the previous report has been developed and tested against the observed thermodynamic properties of (a) pure water, (b) water-hydrocarbon mixtures, (c) water-urea mixtures, and (d) the ternary system water-urea-hydrocarbon. The features of this statistical model can qualitatively account for the behavior of the four systems. The results also indicate that the structured water species bears some functional resemblance to the gas hydrate structures, in that the thermodynamic properties of hydrocarbon solutes in this species are comparable with the enthalpies and entropies of formation of the crystalline hydrates. The unstructured water, on the other hand, shows some of the properties of polar but unassociated solvents. It is hoped to extend the applicability of this model to the study of water-alcohol mixtures. This will probably involve the necessity of numerical solutions to some of the differential equations involved.

2. Hydration and Association in Dilute Solutions of Surfactants.

The results outlined in the previous report were presented at the 1964 Spring Meeting of the ACS and have been submitted for publication in J. Phys. Chem.

Further results on the pH and conductance of sodium dodecyl sulphate solutions in the submicellar concentration range indicate that the association may be due to "acid soap" formation, as is the case for carboxylic acid salts. This would mean that alkyl sulphuric acids are not the strong acids which they are normally considered to be. Evaluation of the results is still in progress.

3. The Properties of Walter-Alcohol Mixtures.

A review article is in the process of being written for Quarterly Reviews (London Chemical Society).

THE STRUCTURE OF THE "HYDRAZONE" OF DINAPHTHOQUINONE

by

Elli Hand, NASA Research Associate in Chemistry, and
Theodore Cohen, Associate Professor of Chemistry

According to Pummerer [Ber. 72, 1623 (1939)], the canary yellow dinaphthoquinone reacts with "hydrazone" to give I, a very insoluble, high-melting material that is black when dry and copper-bronze when crystallized from pyridine. Since these properties seemed at variance with structure I, the compound is under investigation by us.

The "hydrazone" gives a yellow monoacetate, not further acylable, from which the starting material can be regenerated. Elemental analysis and spectral data of the acetate can be interpreted in terms of structure IIa. Our present working hypothesis is that the "hydrazone" has structure IIb. If the color of IIb is due to charge-transfer interactions, the compound should be of considerable interest since the electron-rich and the electron-poor contributors to a charge-transfer complex here are present in the same molecule. This possibility will be investigated. Charge-transfer complexes have recently been of interest because of their electronic properties.

The proximity of the OH and NH groups in IIb is corroborated by the infrared spectrum of a derivative to which structure III is assigned. Attempts to degrade IIb to the known compound IV, whose isolation would unambiguously prove the presence of the nitrogen-containing ring and its relation to the quinone rings, failed. At least four other oxidation products are formed. The structures and reactions of these are being studied. Various model compounds have been prepared. The structure elucidation is also being attempted by unambiguous synthesis. A promising route appears to be via the coupling product of V and benzene diazonium chloride.

I

II a R = $COCH_3$

b R = H

III

IV

V
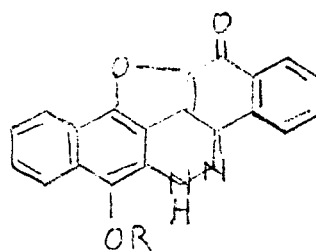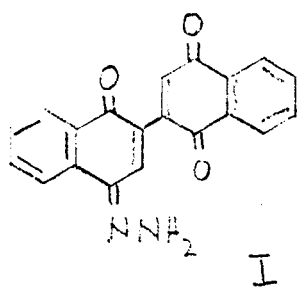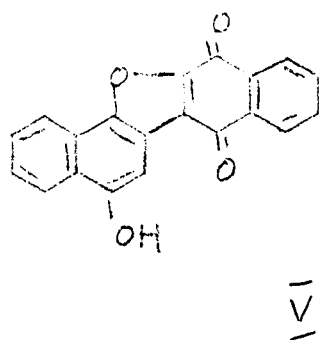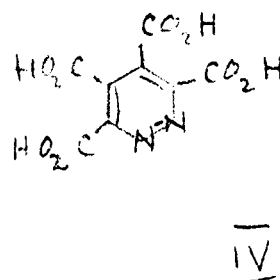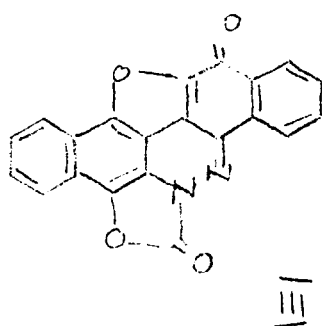
PROGRESS REPORT NO. 2
by
Edgar Inselberg, NASA Research Associate in Chemistry

The following publications, in press or in preparation at the time of the first report, have now appeared.

(a) (with J. L. Rosenberg) Interference of Emission Changes with Fast Absorption Changes in the Flash Spectroscopy of Algae. This paper was included in a symposium volume dealing with the photosynthetic mechanisms of green plants.

(b) Simultaneous Determination of Radioisotope Pairs by the Decay Constant Differentiation Principle (1).

I completed an initial literature review of my current project, "Statistical Inference from Radioactivity Measurements." Over 500 potentially pertinent references were located and read; over 150 were abstracted. Sections of several new texts on radiochemistry and tracer methodology were read. An examination of the most recent catalogs of nuclear equipment companies brought me up to date on recent developments in instrumentation. Several papers pertaining to instrumentation for the detection of radioactivity in space and in the atmosphere were studied. Several conclusions are warranted.

(a) A new model elucidating the nature of the dispersion of radioactivity measurements (1) warrants further study. This study would start with a mathematical derivation of the generalized frequency distribution of radioactivity measurements, of which the Poisson distribution (counting statistics) is but a special limiting case.

(b) The implications of the above model for statistical inference from radioactivity measurements would be investigated.

(c) Since the mathematics involved (e.g., Laplace generating functions, method of maximum likelihood) are above the writer's present attainment, considerable study of mathematical statistics and recent work in applied statistics will be required.

(d) As a result of these readings and the diversity of reprint requests (1), it appears that the work in progress may be of wide applicability.

In accordance with conclusion (c) above, the study of several new textbooks in applied statistics was started. Unpublished data collected by the writer in connection with the work on the simultaneous determination of radioisotope pairs (1) will be used to test the validity of the

mathematical model arrived at and its application to
statistical inference.

(1) Anal. Chem. $\underline{36}$, 568 (1964).

MEASUREMENTS OF CHARGE TRANSFER
AND
IONIZATION CROSS SECTIONS
by
Kotu Lulla, NASA Research Associate in Physics

The following report covers work done in the
laboratory of Professor T. M. Donahue in the Department of
Physics, Space Research Coordination Center, University
of Pittsburgh, since December 1, 1963.

Charge Exchange

$$H^+ \ (100 - 400 \ kev) + H \ (25 \ kev) \rightarrow H^+ + H$$
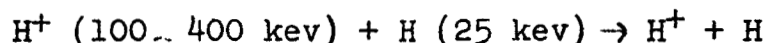
The duoplasmatron ion source has been tuned and
the ion beam analyzed after bending through $90°$ in a
magnetic field. A stable proton beam of one to two
milliamperes has been obtained at 25 kev. A neutralizing
chamber with independent pump station has been designed and
is under construction. This will enable us to charge
exchange a good fraction of H^+ beam. At present, differential
pumping, scattering and detector chambers, each independently
pumped, are being designed.

Electron Loss

A high vacuum gas handling system has been
incorporated in the main apparatus and non-fractionating
diffusion pump and aceton-dry ice trap have been replaced
by 1420 PMC pump (C.V.C.) and liquid nitrogen trap. The
quadruple mass spectrometer has been put into operation
and mass resolution, $\frac{\Delta m}{m}$, of 1/60 has been obtained which
will enable us to distinctively separate masses such as
CO and CN. At present, 30 kev proton beam and the mass
spectrometer are being used to analyze the background as a
function of target gas density.

THE CRYSTAL STRUCTURE OF HYDRATES

by

Thomas Mak, NASA Research Associate in Crystallography

As stated in an earlier report, my study is concerned with the crystal-structure analysis of the double hydrate of tetrahydrofuran and hydrogen sulphide. Complete three-dimensional diffraction data were collected on a Weissenberg camera enclosed in a cold box maintained at $\sim$-20°C. with dry ice.

Preliminary calculations have confirmed the 17 Å cubic water host lattice characteristic of Structure II hydrates (1). The tetrahydrofuran molecules occupy the larger hexahaidecahedra without hydrogen-bonding to the water framework, and the H_2S molecules occupy the dodecahedra, as suggested by von Stackelberg (2). Further refinement of the structure is in progress.

(1) W. F. Claussen, J. Chem. Phys. 19, 259 (1951); M. von Stackelberg and R. H. Müller, Z. Electrochem. 58, 25 (1954).

(2) M. von Stackelberg and B. Meuthen, Z. Electrochem. 62, 130 (1958).

THE BEHAVIOR OF THE HIGH-ENERGY INTERMEDIATES IN ORGANIC SYSTEMS

by

Jack Pinkus, NASA Research Associate in Chemistry, and
Theodore Cohen, Associate Professor of Chemistry

In the study of the nature of highly reactive carbonium ions, their production by expulsion of molecular nitrogen from diazonium ions has furnished numerous opportunities previously for evaluating their physical properties and their chemical behavior towards environmental molecular structure. For generation of these diazonium ions, the use of model precursors, which possess fused rings and several centers of asymmetry in addition to the diazonium ion to carbon bond, allow one to gain insight into the influence of intramolecular effects and solvent interactions on the carbonium ion. Conclusions are drawn by examining the stereochemistry of the product molecules which result from charge neutralization of the carbonium ion by internal electron displacements or by interaction with external nucleophiles.

One ring system which has furnished important data of this type is exemplified by the decalyl amines. The deamination of the cis-2-decalyl amines has been studied by Hückel (1). Conclusions regarding the nature of reactive intermediates in this reaction are based on the relative stereochemistry of a product cis-2-decalol and the starting amine. Dauben and Hoerger (2) have challenged the conclusions of Hückel by presenting evidence that the configurations of the two epimeric cis-2-decalyl amines were misassigned. Nevertheless, Hückel and Stelzer (3) have not accepted Dauben's results as conclusive.

We proposed to resolve this literature conflict before studying other systems. Accordingly we chose to determine the stereochemistry of the cis-2-decalyl amine assigned by Dauben to have the cis-cis configuration. A simple approach would be to convert a cis-2-decalol of known stereochemistry to the cis-2-decalyl amine in an unambiguous fashion. By employing the stereospecific displacement reaction of an alcohol p-toluenesulfonate with liquid ammonia (4), the cis-cis-2-decalyl amine should be obtained from cis-trans-2-decalyl p-toluenesulfonate. Indeed, in this manner we have now shown that the stereochemical assignments for the cis-2-decalyl amines were incorrectly assessed by Hückel. This result therefore confirms the conclusions drawn by Dauben. We propose that this method of stereochemical assignment (high pressure ammonolysis with Walden inversion) is the preferred approach (in the absence of neighboring group interactions) to relating amine and alcohol configurations. The method of Hückel for assigning relative amine and alcohol configurations is thus invalid. The major difficulty in the

aforementioned investigation turned out to be the problem
encountered in obtaining cis-trans-2-decalol not contaminated
with the epimeric cis-cis-2-decalol or the isomeric trans-
trans-2-decalol and the trans-cis-2-decalol. The elusive
supposedly pure cis-trans isomer has only been obtained
previously in small amounts after tedious procedures.
Starting with a commerical mixture of the four decalols,
obtained by reduction of 2-naphthol, containing a few per cent
of the cis-trans and cis-cis isomers, we have attempted to
apply fractional crystallization techniques on a number of
ester derivatives as previously reported. These methods did
not afford pure decalol. Finally we found that the 3,5-
dinitrobenzoates of a partially purified (as the phthalates)
decalol mixture possessed solubility properties which
afforded the desired decalol derivative in a high state of
purity. Also developed was a preparative gas chromatography
procedure for obtaining pure cis-trans-2-decalol.

Studies with carbonium ions derived from diazonium
salts and possessing stabilizing substituents such as aryl or
vinylhave provided important information in recent years.
Some of the patterns of carbonium ion behavior that have
emerged from these investigations indicate to us that a widely
publicized communication (5) in this area may be in
considerable error. We have proposed to reinvestigate the
deamination of 3-phenylallyl amine. Details of its synthesis
are either lacking (5) or given as a series of low yield
steps (6). To facilitate the investigation we have approached
the synthesis of the amine by a new simple route. We
proposed to prepare the unknown 3-phenylallyl isocyanate and
convert the isocyanate group to the amine function. The
first step has already been explored briefly. Based on
nuclear magnetic resonance evidence, the reaction of
cinnamyl bromide with silver cyanate appears to give
excellent yields of the desired isocyanate. Additional work
is in progress in this area and related problems (7).

(1) W. Hückel, Ann. 533, 1 (1937).

(2) W. G. Dauben and E. Hoerger, J. Am. Chem. Soc. 73, 1504
    (1951).

(3) W. Hückel and G. Stelzer, Ber. 88, 984 (1955).

(4) J. L. Pinkus, G. Pinkus, and T. Cohen, J. Org. Chem. 27,
    4356 (1962).

(5) Y. Pocker, Chem. and Ind. 195 (1959).

(6) A. Iliceto and G. Gaggia, Gazz. chim. ital. <u>90</u>, 262 (1960).

(7) J. L. Pinkus and T. Cohen, Interim Report, Oct. 1963.

THERMOLUMINESCENCE IN ALUMINUM-CONTAINING QUARTZ
by

M. Schlesinger, NASA Research Associate in Physics

This work is concerned with the thermoluminescence in x-irradiated aluminum-containing quartz, both doped with germanium as well as germanium-free. The general glow curves and their spectral composition have been investigated. A germanium-doped crystal exhibits two main glow peaks, one at 460 °K and another at 600 °K. The germanium-free sample exhibits a main glow peak at 570 °K. All these peaks have been found to have the same spectral composition, which consists of a broad band (half width of about 0.58 eV) peaking at about 485 mμ.

The crystals used were Clevite $(33C-4_2)$ germanium-doped and Bell (R-537) germanium-free quartz crystals. Both crystals contain aluminum. Typical results of emission analyses on portions of these crystals are given in reference (1), Table 1. X-irradiation was carried out with a Dunlee x-ray tube (with a tungsten target) operated at 50 KVP and 15 mA. The general glow curves were recorded essentially in the same way as described elsewhere (2). The spectral composition, however, of the glow which is fairly low in intensity, was taken with the colored crystal heated in the vacuum cryostat (2) with its window in nearest access to the entrance slit of a Leiss single monochromator (relative aperture of 1:6.2). An RCA 1P 28 type photomultiplier was attached to the exit slit of the monochromator. The output of the photomultiplier was connected to the y terminals of a Tektronix 555 type dual beam oscilloscope, through a type-D plug-in unit. The wavelength drum in the monochromator was driven to and fro over the desired spectral interval by a General Radio type 1750-A mechanical sweep drive. The proportional voltage output of the sweep drive was connected to the x terminals of the scope. Photographs of the oscilloscope trace were taken with a Polaroid camera.

Curve (a) in Fig. 1 is the glow curve of the germanium-doped crystal after x-irradiation for 40 minutes at room temperature. (The vertical scale has been reduced by a factor of 20.) The heating rate was about 10°/min. The strongest peak appears at about 600 °K, a weaker peak occurs at about 460 °K. Curve (b) in Fig. 1 is the same plot (but at full scale) for the germanium-free sample. The strongest peak in this case appears at about 570 °K. It is of interest to note, that while the intensity ratio between this peak and the peak at 600 °K in curve (a) is about 1:100, the optical density at the "Aluminum" absorption bands ($\simeq 450$ mμ) is of the same order of magnitude in both cases.

Fig. 2 shows the spectral composition of the glow in both the 460 °K and 600′ °K glow peaks of the germanium-doped

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crystal. The same spectral composition is found in the
570 °K peak of the germanium-free crystals. The half width
of the emission band is the same for all three glow peaks.

Electric conductivity measurements performed on the
germanium-doped crystal show no detectable current peaks
during the thermoluminescent light emission.

The fact that the spectral composition of the
thermoluminescence (Fig. 2) is the same for both samples implies
that the emission is due to the same optical transition in
both samples. On the other hand the maxima of the glow
curves occur at different temperatures (Fig. 1). An
interpretation consistent with these facts is as follows:
during x-irradiation electrons removed from aluminum sites (3)
(present in both crystals) are trapped at other sites. These
sites have previously been identified in germanium-doped
quartz (in part, at least) as substitutional germanium
atoms (4); in germanium-free quartz the electron traps have
not been identified. Heating frees the trapped electrons at
temperatures characteristic of the electron traps. The
released electrons in both germanium-doped and germanium-free
crystals recombine with the holes at the aluminum sites.
The emitted light is associated with the recombination
process which is the same in both crystals.

The higher intensity of the thermoluminescence in
the germanium-doped sample is of interest. This implies
that the presence of germanium in the crystal not only provides
trapping sites for electrons, but also enhances the proba-
bility of radiative recombination of electrons and holes.
This conclusion is based on the assumption that the number of
trapped holes is about the same in both crystals, since the
optical density in the 450 mμ band attributed to the trapped
holes (5) is about the same and one assumes proportionality
between optical density and number of color centers, as is
the case with alkali halides.

The lack of thermally stimulated current in turn
might imply that the germanium impurity is in spacial
association (6) with the aluminum impurity, thus being able
to influence the recombination process as stated above.

It is a pleasure to acknowledge with thanks the
encouragement and valuable suggestions made by Professor
John H. Anderson.

(1) A. Halperin and J. E. Ralph, J. Chem. Phys. 39, 63 (1963).

(2) M. Schlesinger, Ph.D. thesis, The Hebrew University of
    Jerusalem, 1963 (unpublished).

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(3) In the O'Brien (5) model the hole is assumed to reside predominantly on an oxygen atom bound to the aluminum.

(4) J. H. Anderson and J. A. Weil, J. Chem. Phys. $\underline{31}$, 427 (1959).

(5) M. C. M. O'Brien, Proc. Roy. Soc. $\underline{A231}$, 404 (1955).

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Fig. 1   Glow curves as taken (a) from germanium-doped Clevite (33C-4_2) Quartz crystal (b) germanium-free Bell (R-537) crystal. Both irradiated for 40 min. at room temperature, heating rate about 10°/min. [curve (a) 20X reduced].

Fig. 2   Re-plot of the oscilloscope trace photographs of the spectral composition of the glow at 460 °K, 600 °K peaks in the (33C-4_2) and the 570 °K peak in the (R-537) Quartz crystals.
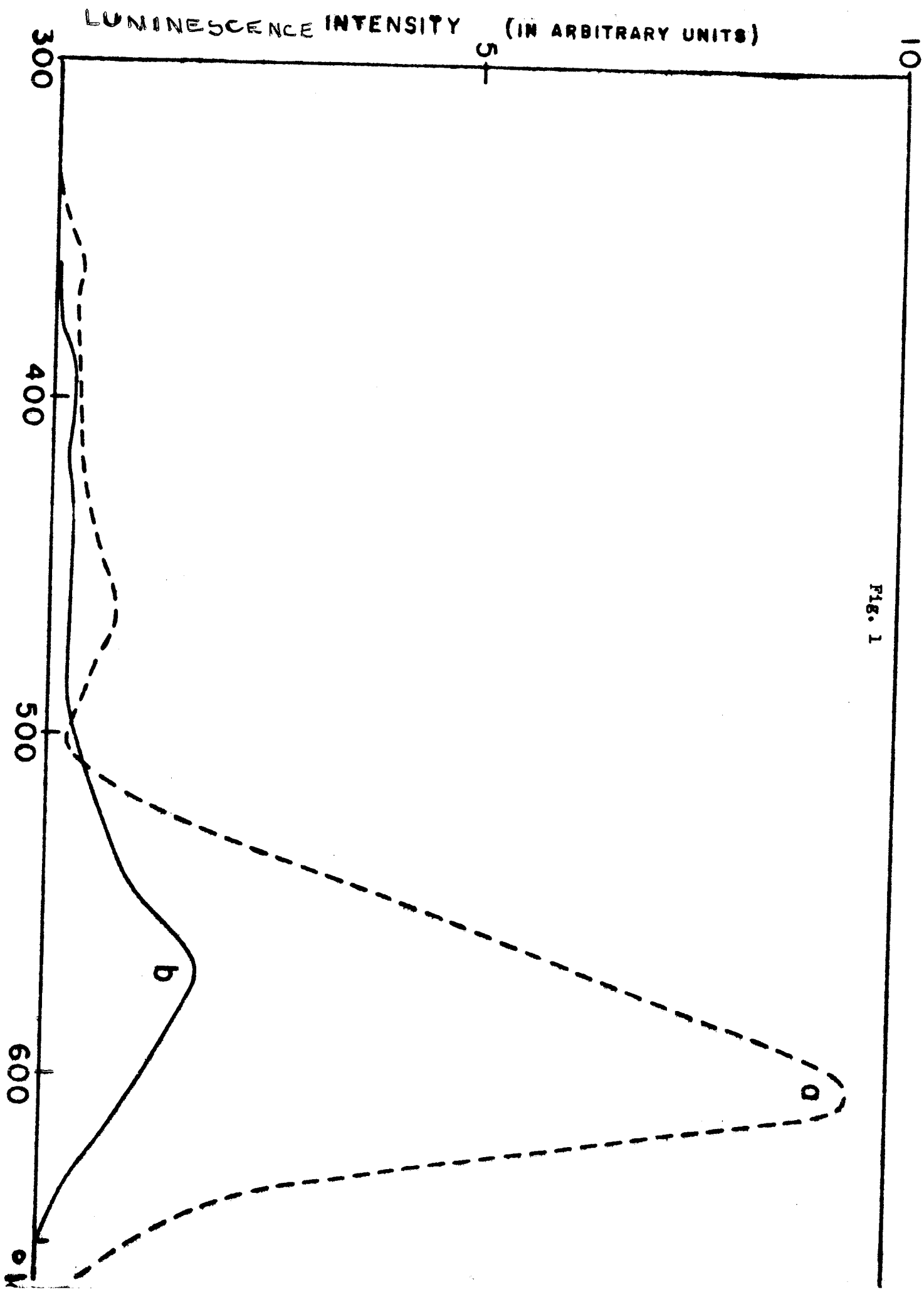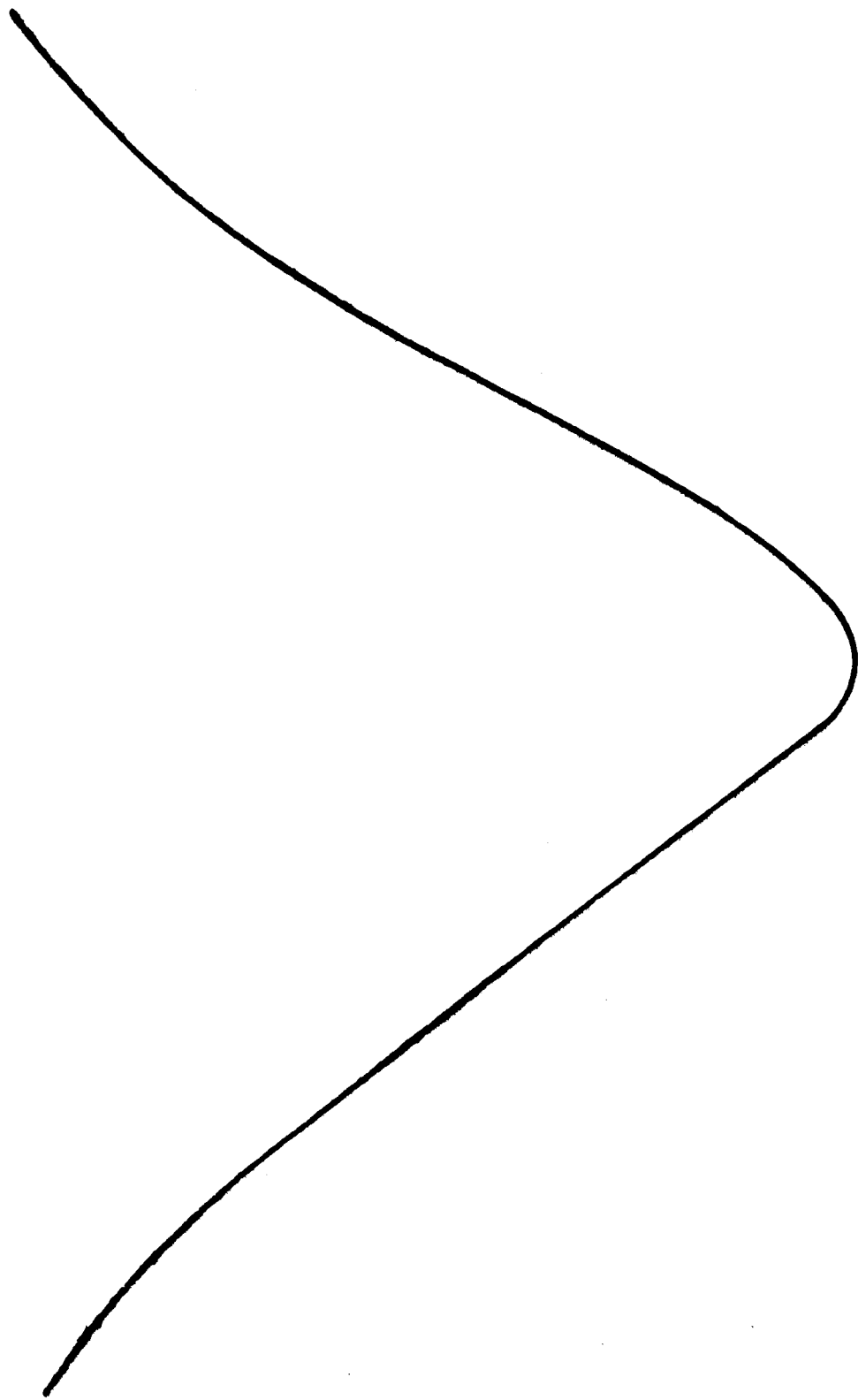
LUMINESCENCE INTENSITY (IN ARBITRARY UNITS)

Fig. 1

LUMINESCENCE INTENSITY (IN ARBITRARY UNITS)

FIG. 2

A STUDY OF SOME TYPES OF CHEMICAL BONDING
by
John Tanaka, NASA Research Associate in Chemistry

A synthesis of completely deuterated trimethylamine was undertaken in order to be able to assign the boron-hydrogen infrared frequencies of boron hydride-amine adducts.

Two model syntheses were developed. One entailed a sequence of reactions, the first steps of which involved the reaction of triethylamine with methyl bromide, the conversion of the product to the quaternary ammonium hydroxide, followed by a pyrolytic elimination of ethylene. The above sequence repeated twice more produced the desired product. Another approach involved reacting methyl bromide with ethylamine in the presence of silver oxide. The ethyltrimethylammonium hydroxide formed was filtered, separated from water, and pyrolyzed. When the second of the above reactions was carried out with deuterated methyl bromide, a hydrogen-deuterium exchange was found to have taken place.

The nature of the hydrogen-deuterium exchange was studied, using complete deuterium oxide media and the Hoffman elimination of the quaternary ammonium deuteroxide. The mechanism has been shown to involve a nitrogen ylide during the pyrolytic elimination reaction. Deuterium was always found to be introduced into the ethylene eliminated and hydrogen was always found to be introduced into the methyl groups of the trimethylamine.

Methods are being worked out to synthesize the deuterated trimethylamine from tetramethylammonium deuteroxide. Improvement in yields are currently being sought.

A paper is being planned for the September American Chemical Society Meeting in Chicago.

GENETIC AND BIOCHEMICAL EFFECTS OF RADIATION ON SOMATIC CELLS
by
S. Venketeswaran, NASA Research Associate in Biology

Stock cultures of green and albino callus of tobacco are maintained with subculturing at 4-6 week intervals. The data from the first set of experiments indicate that maximum growth (fresh weight or dry weight) of both green and albino takes place on a culture medium supplemented with indoleacetic acid (IAA) and 2,4-dichlorophenoxyacetic acid (2,4-D) both at 1×10^{-6} M or with IAA and kinetin both at 1×10^{-6} M. Preliminary observations reveal that the presence of 2,4-D in the culture medium can affect pigment production in the green strain.

From these routine cultures, it has been possible to isolate the green strain as "visibly green cultures" both in solid and in liquid culture with the green color being maintained in continued subcultures by growing the cultures under very diffuse light conditions thus preventing photo-destruction of the chlorophyll pigments. Spectrophotometric determinations of the pigment contents of the green callus cultures show no difference in pigment components from that of the intact plant. The liquid culture is highly friable and maintains a very active growth rate producing a very good suspension of cells and cell-aggregates. One ml. inoculum of such a liquid suspension when plated on an agar plate produce visibly green colonies within 2 weeks. The smallest of such a visibly green colony can weigh as little as 4-6 milligrams. These small colonies when extracted with 80 per cent acetone show detectable pigment separation into the various components by thin layer chromatographic techniques. Thus the capacity for pigment production in such small cell colonies is being retained indicating the stability of the gene for chlorophyll production in culture.

The albino strain also maintains a very active growth rate both in solid and in liquid cultures and produces visible albino colonies when plated on agar plates. In one culture flask growing in very diffuse light, large patches of "chlorophyllous areas" have appeared indicating that "somatic backmutation" can occur in proliferating cells of the callus tissue too. Attempts are in progress to maintain this "strain" stable in continuous cultures using various low-intensity illuminations. Attempts are also directed to evaluate development of mutated colonies which are physiologically capable of chlorophyll production from albino suspension cultures by plating techniques.

Intact albino plants grown as "normal" seedlings have been growing very well in big culture vessels as high

as 12 inches. Continued efforts are directed to "graft"
them to mature green tobacco plants in greenhouse in order
to photoinduce flowering.

Ten-day old germinated green and albino tobacco
seedlings were irradiated for different dosages in a Cs^{137}
source. Periodical observations are being made on the
growth of the leaves in the albino seedlings for changes in
number of "green" patches and other growth phenomena.
Suspension cultures of green and albino cells were also
irradiated with ultraviolet and Cs^{137} source and plated on
agar plates and observations are in progress.

STABILITY OF PARTIAL DIFFERENTIAL EQUATIONS
by
William Vogt, NASA Research Associate in
Electrical Engineering

A Lur'e Problem in Partial Differential Equations:

Consider the system

$$\frac{\partial \underline{\mu}}{\partial t} = \underline{A}\,\underline{\mu} + \underline{b}\,f(\sigma) + \underline{B}\,\frac{\partial \underline{\mu}}{\partial x}$$

$$\frac{\partial \sigma}{\partial t} = \underline{d}'\,\underline{\mu} - r\,f(\sigma) \qquad\qquad (1)$$

where $\underline{\mu}(0, t) = \underline{\mu}(1, t) = 0$ and $\sigma(0, t) = \sigma(1, t) = 0$, and where $f(0) = 0$ and $s\,f(s) > 0$, $s \neq 0$. $\underline{\mu}$, $\underline{b}$, $\underline{d}$ are n-vectors; $\underline{A}$, $\underline{B}$ are $n + n$ matrices.

For a Lyapunov functional, choose

$$V(\underline{U}) = \int_0^1 \left[\underline{U}'\,\underline{Q}\,\underline{U} + \int_0^\sigma f(s)\,ds \right] dx$$

Then

$$\dot{V}(\underline{U}) = \int_0^1 \left\{ \underline{U}'\,(\underline{A}'\,\underline{Q} + \underline{Q}\,\underline{A})\,\underline{U} + f(\sigma)\left[\underline{U}'\,\underline{Q}\,\underline{b} + \underline{b}'\,\underline{Q}\,\underline{U} + \underline{d}'\,\underline{U} \right] \right.$$
$$\left. - r\,f^2(\sigma) + \underline{U}_x'\,\underline{B}'\,\underline{Q}\,\underline{U} + \underline{U}'\,\underline{Q}\,\underline{B}\,\underline{U}_x \right\} dx$$

Along with this system, consider the Lur'e problem for ordinary differential equations given by

$$\dot{\underline{y}} = \underline{A}\,\underline{y} + \underline{b}\,f(\rho)$$

$$\dot{\rho} = \underline{d}'\,\underline{y} - r\,f(\rho) \qquad\qquad (2)$$

For (2), consider the Lyapunov function

$$W(\underline{y}) = \underline{y}'\,\underline{Q}\,\underline{y} + \int_0^\rho f(s)\,ds$$

the derivative of which is

$$\dot{W}(\underline{y}) = \underline{y}'\,(\underline{A}'\,\underline{Q} + \underline{Q}\,\underline{A})\,\underline{y} + f(\rho)\left[\underline{y}'\,\underline{Q}\,\underline{b} + \underline{B}'\,\underline{Q}\,\underline{y} + \underline{d}'\,\underline{y} \right]$$
$$- r\,f^2(\rho)$$

The following theorem is an immediate consequence.

Theorem:

A sufficient condition for the asymptotic stability of the null solution of (1) is

(i) $W(\underline{y}) > 0$, $\underline{y} \neq \underline{0}$

(ii) $\dot{W}(\underline{y}) < 0$, $\underline{y} \neq \underline{0}$

(iii) $\underline{B}'\,\underline{Q} = \underline{Q}\,\underline{B}$